Spin-Off company of Italian National
Research Council – **CNR**
Materials Division
Via Cocchi 7, 56121 Pisa – Italy

Combination of mineral fillers 3rd phase evolution: Opportunities and drawbacks for the CPR complying cables

Camillo Cardelli - Marco Badalassi

IPOOL Pisa (Italy)

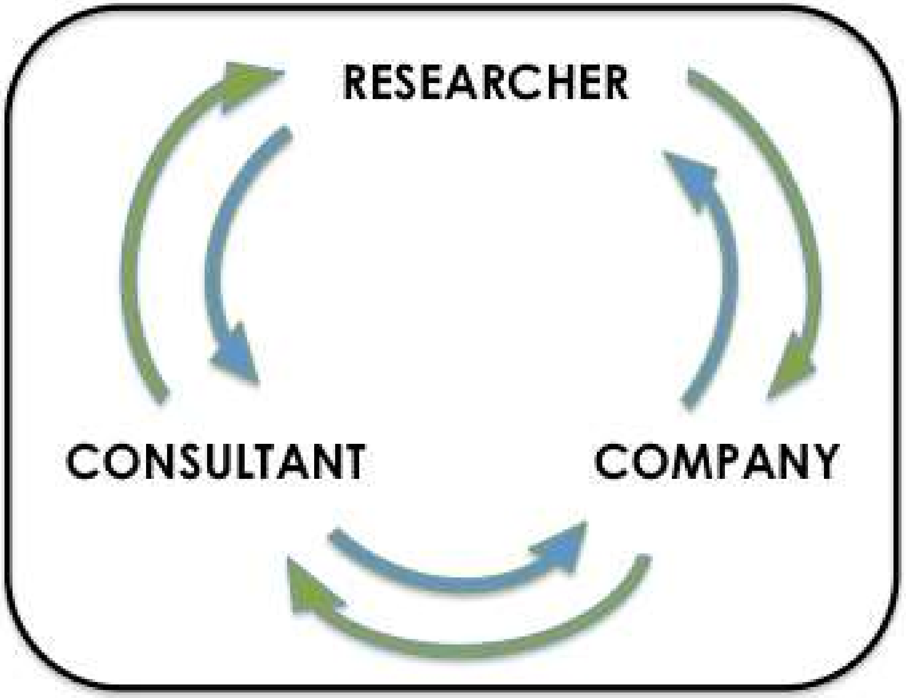
FIRE RESISTANCE IN PLASTICS 2018 - Cologne, Germany

IPool srl

IPool is a spin-off company of National Council of Research institute (CNR) of Italy. It has been established in July 2011 and it is founded on the strictly connected work of researchers, professionals and industrial companies.

Mission

Scientific and industrial development of know-how and applications regarding chemical and physical properties of materials and specific measurements methods and instruments.



Technical consulting about design, industrialization, and marketing of raw materials and compounds with high performances and low environmental impact. Specialized services of Applicative Research and Technological Development for companies operating in safe-materials (**flame retardant and low smokes**) and recycling materials (**circular economy**).

Typical cable formulations

- Polymers (EVA – POE – LLDPE)

- Coupling agents (maleic grafted polymers or silane)

- Mineral Fillers (flame retardant or not)

- Additives (stabilizer, process aid, hydrophobic, plasticizer, crosslinking, flame retardant ...)

Mineral fillers for cables

Synthetic

Aluminium tri-hydroxide (ATH)

Aluminium mono-hydroxide (Böhmite - AOH)

Magnesium di-hydroxide (MDH)

Zinc borate

Natural

Brucite (Magnesium di-hydroxide – MDH)

Magnesite (magnesium carbonate)

Huntite / Hydromagnesite (magnesium carbonate + magnesium hydroxy carbonate)

Colemanite (Calcium borate)

Calcium carbonate - Dolomite

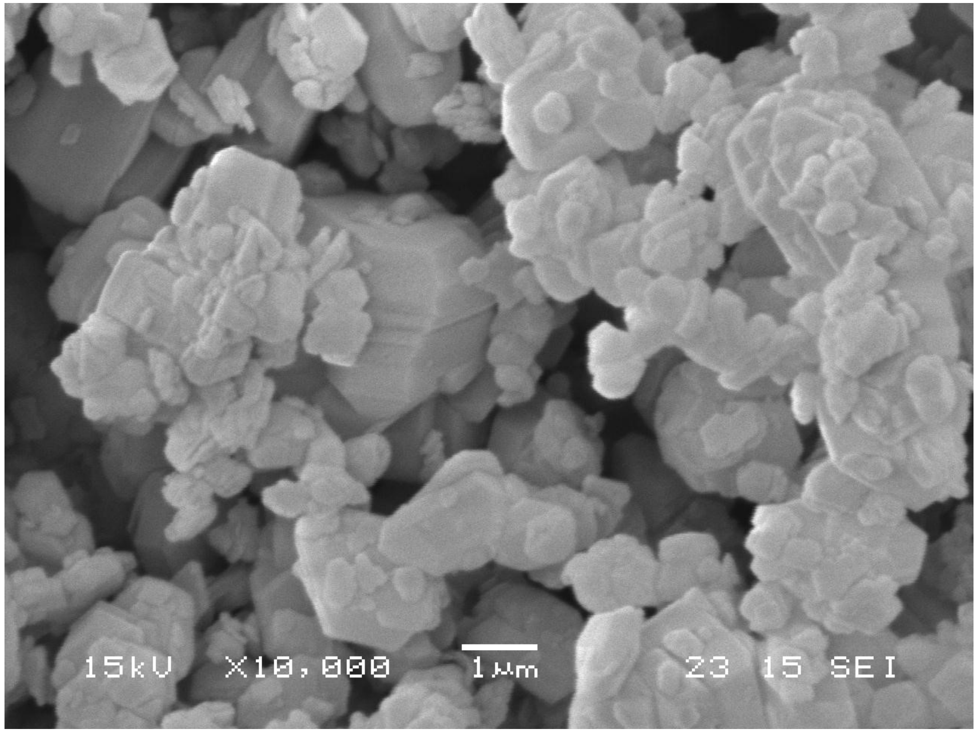
Talc - Sepiolite

Aluminium tri-hydroxide (ATH)

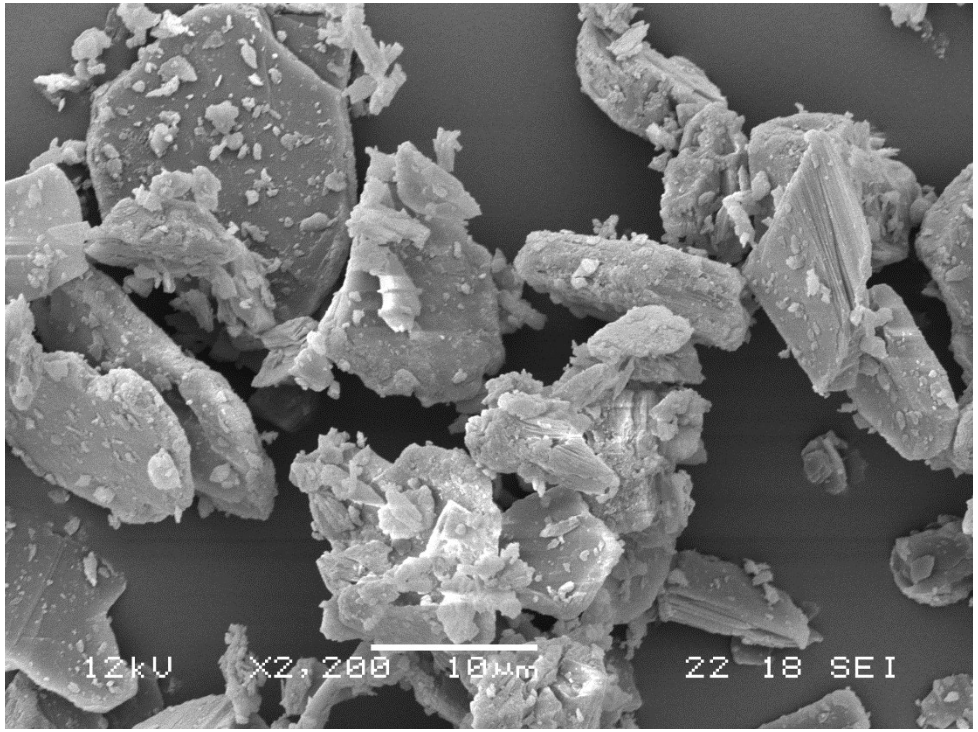
It's the main FR filler in cable industry for HFFR compounds

Used in EVA and PE copolymers, where compounding and extrusion are below 180°C

Most used granulometry in cables compounds is d_{50}=2-3µm with surface area 3-5 m^2/g



Fine precipitated ATH (pp-ATH)



Coarse Milled ATH

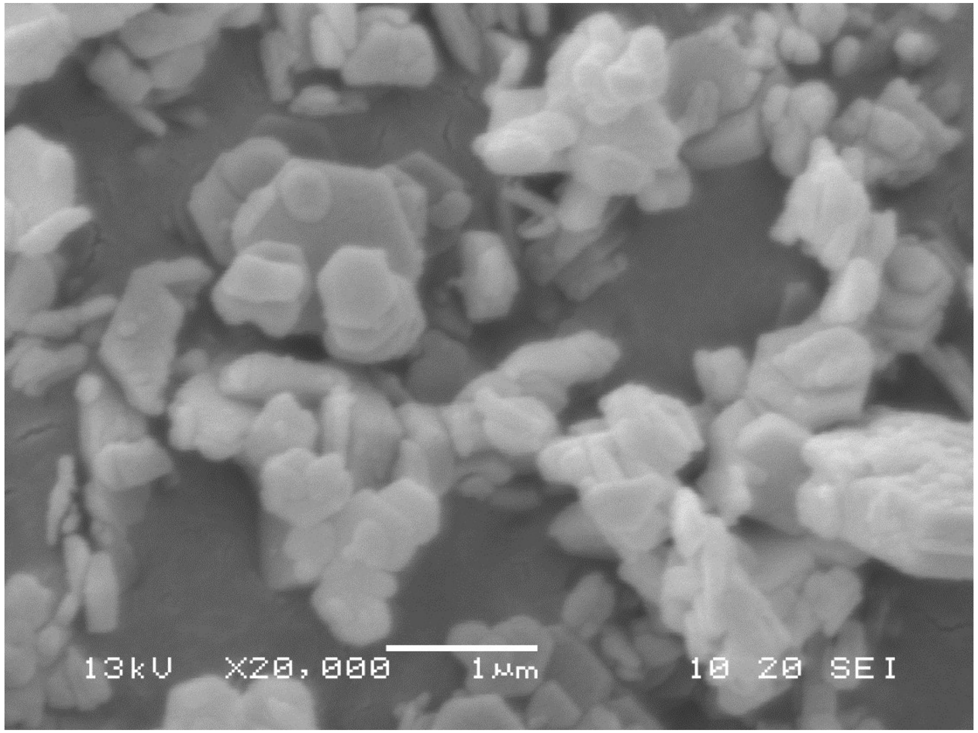
Magnesium Di-Hydroxides (MDH)

Lower volumes in the market vs ATH, mainly for price and availability

Available in different quality levels (granulometry, crystal shape, coatings,….)

Typical granulometry is d_{50}=0,7-3,5 µm with surface area 3-12 m^2/g

Used in all polyolefin where compounding and extrusion at T>200°C



Crystallized MDH (pp-MDH)

Precipitated MDH

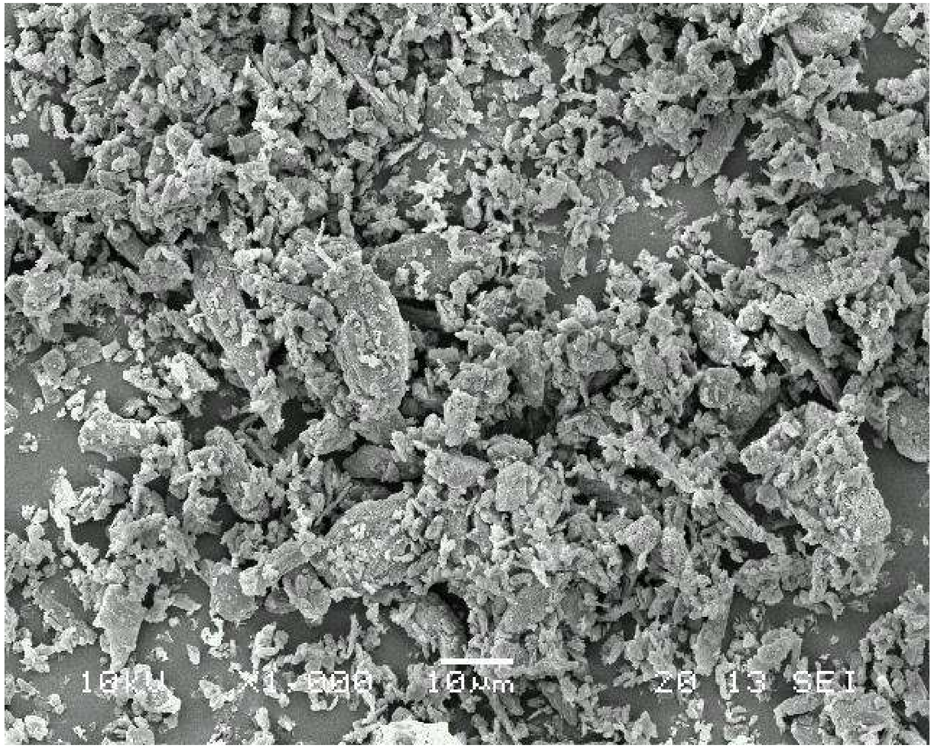
Milled Brucite (natural MDH)

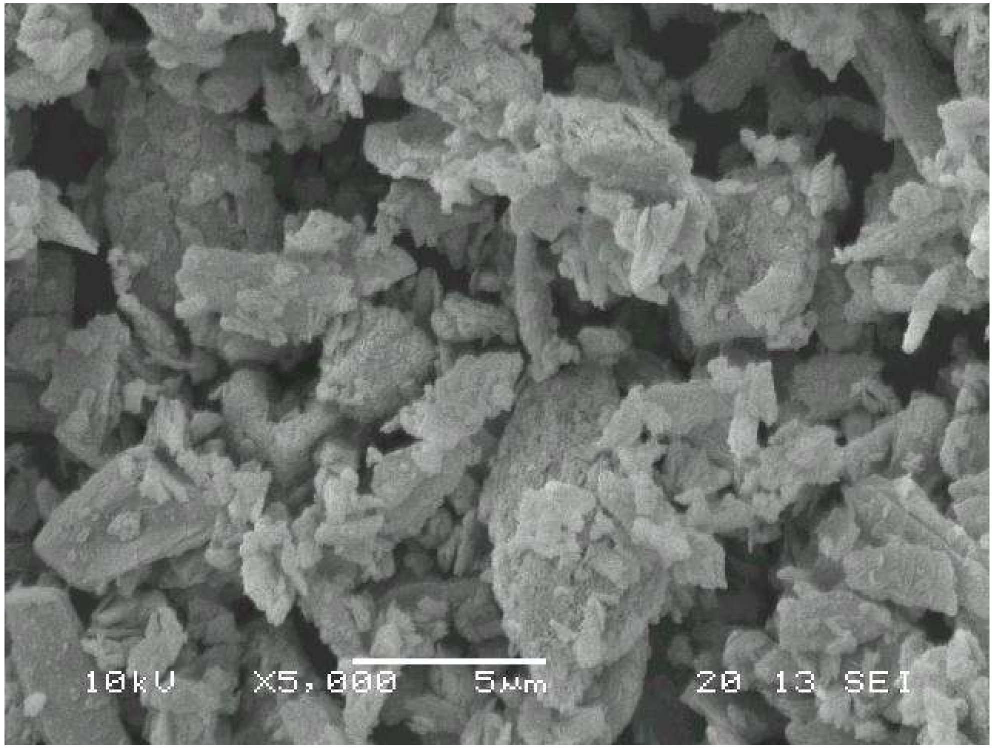
It's the second main FR filler in cable industry

Typical composition is 90-92% MDH, 5-8% Magnesite+Calcite and <2% other minerals

Many grades available with granulometry d_{50}=2-20 µm with surface area 3-10 m^2/g

Surface coated grades with stearic derivatives and silanes





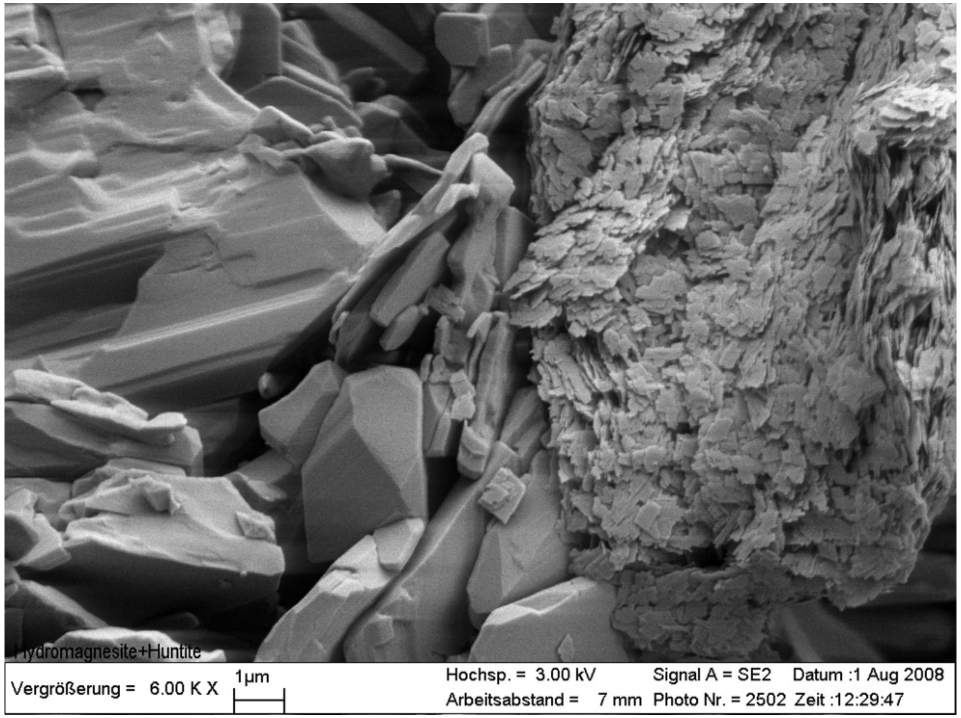
Huntite/Hydromagnesite

Natural blend of Magnesium Carbonate (Huntite) and Magnesium Hydroxy Carbonate (Hydromagnesite)

Typical composition is 60-70% Huntite, 30-40% Hydromagesite, 5-10% Calcite and <2% other minerals

Lower thermal stability than MDH and higher than ATH: T (decomp.) 220-230°C

Platy structure of the Huntite fraction



Synthetic fillers: pros and cons

PROS

- Good mechanical and rheological properties
- Processability – very good surface quality
- Colour
- Electrical properties

CONS

- Relatively high cost, continuously increasing
- Periodical shortage availability in the market due to fast growing demand
- Low temperature of decomposition (only for ATH)

Milled hydrated fillers: pros and cons

PROS

- Relatively low cost, much more stable
- Large availability
- Similar flame retardancy than synthetic one
- Most of the CONS can be overcome by applying a surface coating

CONS

- Lower mechanical properties
- Rough/less smooth surface at high speed of extrusion
- Water uptaking (Hygroscopicity)
- High specific surface giving less easy compounding and higher compound viscosity
- Combined effect of high hygroscopicity and high viscosity could create some porosity into extruded cables due to water release and high shear into extruder.
- Off white / light grey colour

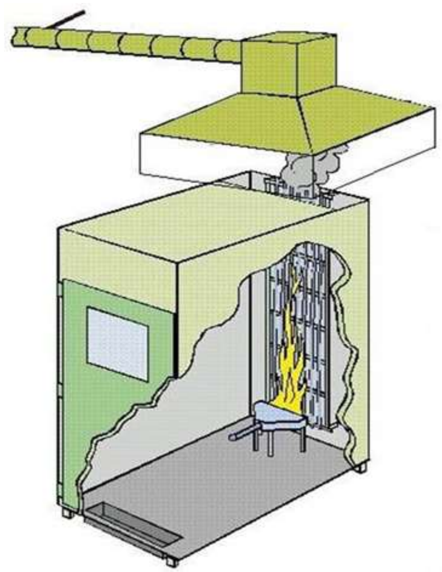
Evolution in the use of mineral fillers

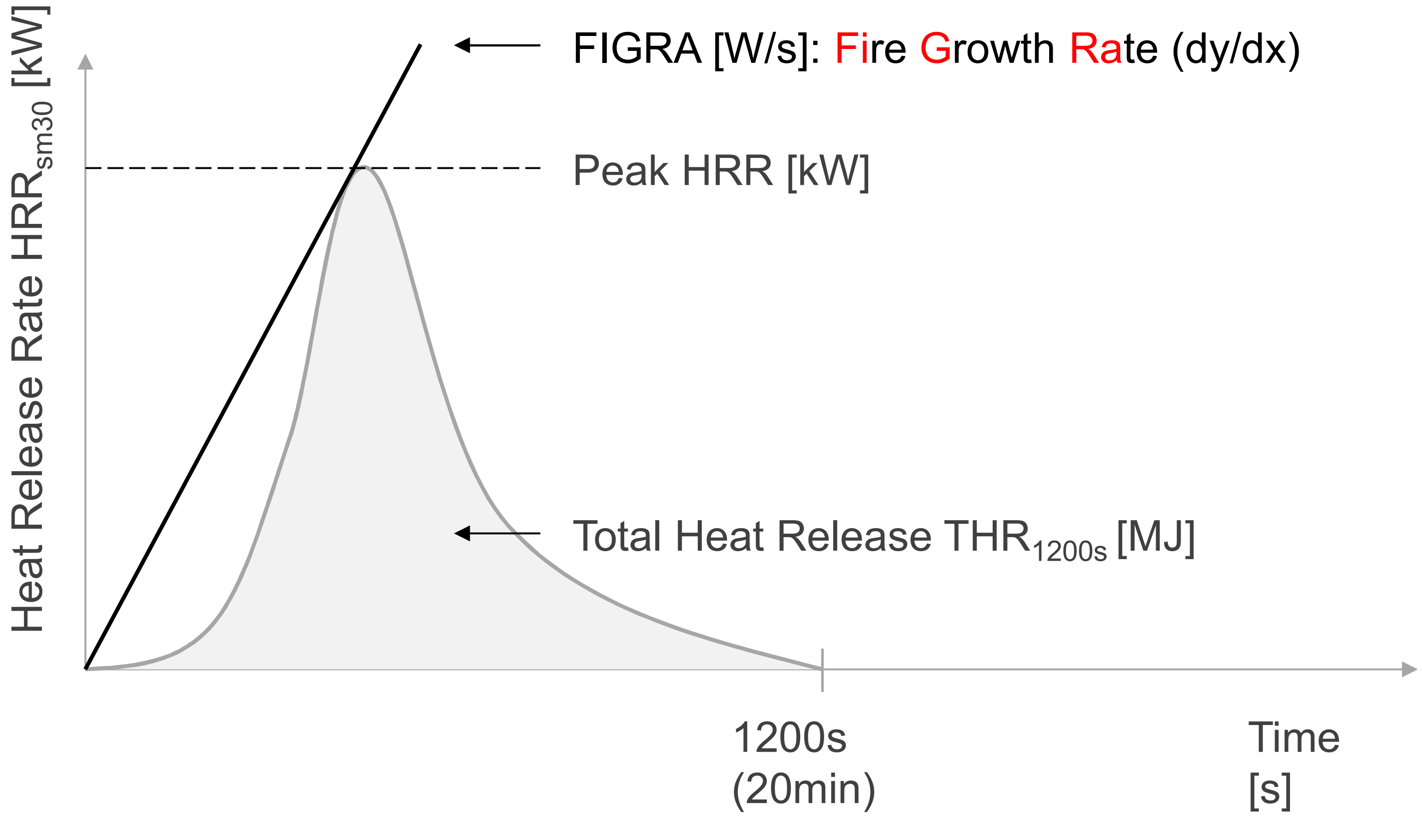
1. 1980-2000: HFFR formulations using a single type of metal hydroxide: fine precipitated ATH (pp-ATH) or fine precipitated MDH (pp-MDH).

2. 2000-2010 Combination of two fillers:
   - Combination of pp-ATH with milled natural MDH (n-MDH) in order to improve flame retardancy and, at the same time, to have competitive HFFR compound.
   - Combination of pp-ATH with some fine milled $CaCO_3$ in EVA based recipes
   - Combination of n-MDH with some fine milled $CaCO_3$ in POE based recipes

3. Combination of 3 fillers: rarely technologists investigated and applied combination of more than 2 fillers in order to optimise performances, processability and sustainability of compounds.

CPR fire test method





Limited Oxygen Index is not any more useful to classify flame resistance (FR) of HFFR compounds. **Rate of Heat Release (RHR) and Smoke Release (SEA)** became the most important parameters to classify the FR of compounds.

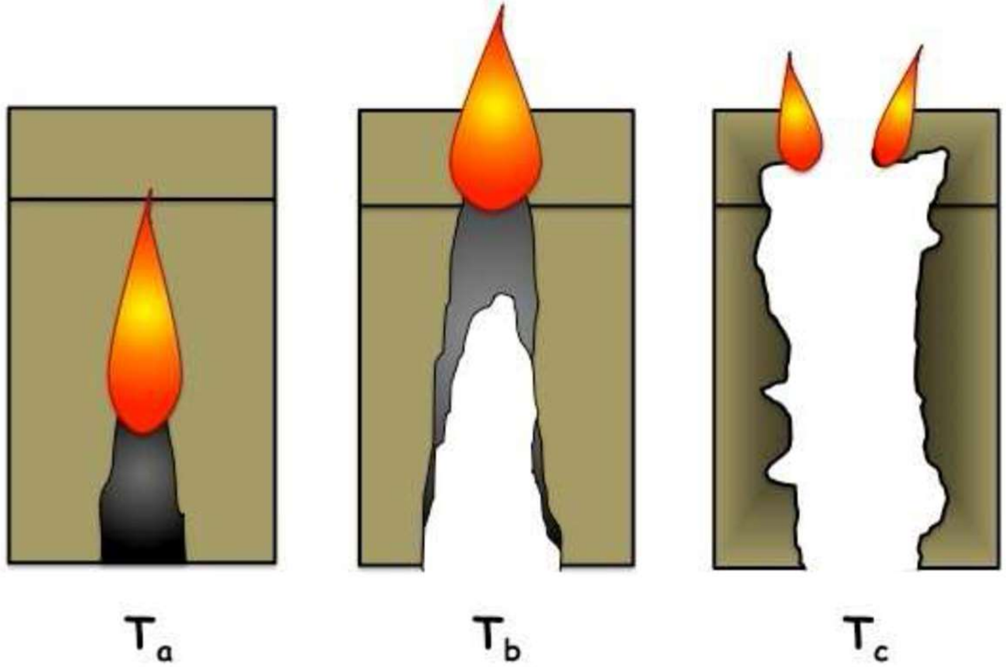
CPR classification

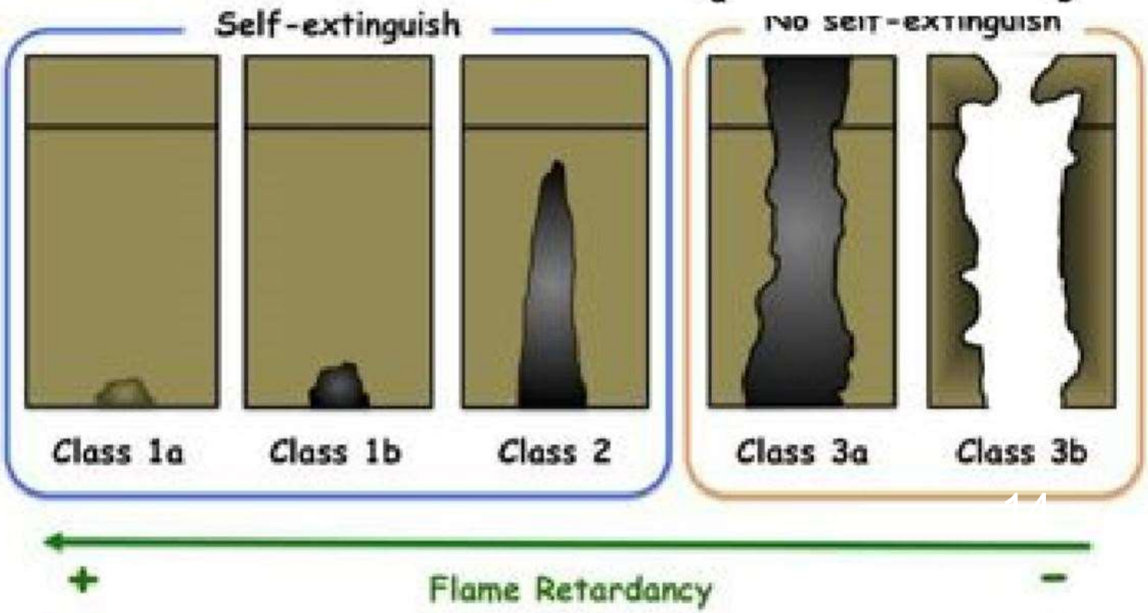
Classification	Class	Test method	Evaluation criteria	Additional evaluation criteria
Non-inflammable	Aca	EN ISO 1716 (bomb calorimeter)	PCS ≤ 2.0MJ/kg	
Low risk of fire	B1ca	EN 50399 (30kW ignition source)	FS ≤ 1.75m and THR_{1200s} ≤ 10MJ and PHRR ≤ 20kW and FIGRA ≤ 120W/s	**s1** (**s1a** or **s1b**), **s2** or **s3** **d0**, **d1** or **d3** **a1**, **a2**, **a3** or no declaration
		EN 60332-1-2	H ≤ 425mm	
	B2ca	EN 50399 (20.5kW ignition source)	FS ≤ 1.50 m and THR_{1200s} ≤ 15 MJ and PHRR ≤ 30kW and FIGRA ≤ 120W/s	
		EN 60332-1-2	H ≤ 425mm	
	Cca	EN 50399 (20.5kW ignition source)	FS ≤ 2.0 m and THR_{1200s} ≤ 30 MJ and PHRR ≤ 60kW and FIGRA ≤ 300W/s	
		EN 60332-1-2	H ≤ 425mm	
	Dca	EN 50399 (20.5kW ignition source)	THR_{1200s} ≤ 70MJ and PHRR ≤ 400kW and FIGRA ≤ 1300W/s	
		EN 60332-1-2	H ≤ 425mm	
Standard cable	Eca	EN 60332-1-2	H ≤ 425mm	
No classification	Fca			

Laboratory vertical fire test

Modified DIN 4102 B2 Vertical burning test

Specimen dimension: 200 x 100 x 1,5 mm
Flame application: 120 sec
Flame application: 45° from the bottom of the specimen





Laboratory vertical fire test

Group	Parameters	UM
Flame evolution	Time 1. Top of the flame to high limit of the specimen (19 cm)	sec
	Time 2. Flame base to graduation line (15 cm)	sec
Self-extinction	Self-extinction	YES/NO
	Time to self-extinction	sec
Dripping	Presence of burning drops	YES/NO
	Time to dripping start	sec
	Type of dripping	-
Flame dimension	Maximal flame height	cm
	Flame width at graduation line (maximum width)	cm
Solid phase behavior	Notes	-

Laboratory vertical fire test

Group	Parameters	UM	1	2	3	4	5
Flame evolution	Time 1. Top of the flame at high limit (19 cm)	secs	225	150	200	90	110
	Time 2. Flame base to graduation line (15 cm)	secs	375	345	310	250	220
Self-extinction	Self-extinction	YES/NO	NO	NO	NO	NO	NO
	Time to self-extinction	secs	-	-	-	-	-
Dripping	Presence of burning drops	YES/NO	NO	NO	YES	YES	YES
	Time to dripping start	secs	-	-	240	60	60
	Type of dripping	-	-	-	Big particles	Medium burning particles	Small particles
Flame size	Maximal flame height	mm	230	250	320	280	350
	Flame width at graduation line (maximal width)	mm	45	55	75	70	60
Solid phase behaviour	Notes	-	Slow ignition Strong char formation. Small deformation	Fast ignition Dripping and high deformation of the specimen.	Slow ignition Dripping of one big particle. Medium deformation of the specimen.	Fast ignition Dripping and high deformation of the specimen.	Fast ignition Dripping and high deformation of the specimen.
IPool FR classification		Points	5	3,5	1,5	0,5	0,5

Influence of Hydrated Fillers on fire behaviour of EVA/POE recipes

Filler	Flame spread (HRR)	Smokes (SEA)	Stop Dripping / char cohesion	LOI (%O_2)
pp-ATH	√	√√	√	√√
pp-MDH	√√	√√	√√	√√
Fine milled brucite	√√	√√	√√	√
Milled huntite/ hydromagnesite	√	√√	√√	√
Calcium carbonate	×	=	××	×
Böhmite d_{50}=1-2 mµ	=	√	=	√

Targets for new HFFR compounds

1. High compounding/production speed, as close as possible to PVC compounds

- Low viscosity compounds
- Thermally stable fillers (>200°C) $\Rightarrow$ **ATH-FREE**
- Low-hygroscopicity compounds

2. Cost-competitive and more sustainable formulations

- Possibility to use wide range of natural and synthetic fillers
- Synergistic combinations

EVA formulations: filler selection

Good FR behaviour

- Fine milled brucite (uncoated and coated grades)
- Huntite: platy structure for stronger char formation

Good processability, surface quality and mechanical properties

- Böhmite (coated and uncoated grades): mineral processing aid, synergistic behaviour with MDH for char forming and elongation at break
- Calcium carbonate
- Dolomite

Effect of polymers and additives

Polymers

EVA: Higher vinyl acetate content contributes to char forming

POE: lower density contributes to accept more fillers

Additives

Hydrophobic MB: reduce hygroscopicity of compounds (less water uptaking and better electrical properties)

Silicon MB: improve processability and surface smoothness, without affect burning

Filler coating: reduce hygroscopicity and improve filler dispersion

Formulations: example 1

Components	Trade name	Producer	Dosage (phr)	Dosage (%)
EVA 28 – MFI 3	Elvax 265	DuPont	40	14,8
EVA 18 – MFI 1	Elvax 470	DuPont	40	14,8
VLDPE – MFI 4	Clearflex CLD0	Versalis	10	3,7
Maleic coupling agent	Compoline CO/UL 05	Aurserpolimeri	10	3,7
Silicon MB	Silmaprocess AL1142A	Silma	3	1,1
Stabilizer	Silmastab AE1527	Silma	1,5	0,6
Hydrophobic MB	Silmastab AX2244	Silma	1,5	0,6
Total filler dosage	-	-	165	61

Example 1: results /1

Fillers	MDH AOH CaCO3	MDH AOH dolomite	MDH AOH S-dolomite
Stearic Coated brucite – Ecopiren 3,5C	31	31	31
Böhmite – Aluprem TB dry	15	15	15
Calcium carbonate – Polyplex 0	15		
Milled dolomite d_{50}=3		15	
Silane coated dolomite d_{50}=1,5			15
Properties			
Tensile strenght (MPa)	10,5	10,8	11,3
Elongation at break (%)	**171**	142	144
MFI 21,6 kg @ 190°C (g/10 min)	8	9	8
LOI (%)	34	**37**	**36**

Example 1: results /2

Properties in vertical fire test	**MDH AOH $CaCO_3$**	**MDH AOH dolomite**	**MDH AOH S-dolomite**
Time 1. Top of the flame 20 cm (s)	120	110	**160**
Time 2. Bottom of the flame to grad. line (s)	310	300	**Not reached**
Self extinguish (YES/NO)	NO	NO	**YES**
Presence of burning drops (YES/NO)	**YES**	**YES**	**YES**
Starting time of burning drops (s)	120	**60**	**80**
Dimension of burning drops	small	small	small
Flame height (cm)	25	26	23
Flame width at graduation line (cm)	5	4	4

Formulations example 2

Components	Trade name	Producer	Dosage (phr)	Dosage (%)
EVA 28 – MFI 3	Elvax 265	DuPont	70	25,8
LLDPE – MFI 4	Exceed 3518	Exxon Chemical	20	7,4
Maleic coupling agent	Compoline CO/UL 05	Auserpolimeri	10	3,7
Silicon MB	Silmaprocess AL1142A	Silma	3	1,1
Stabilizer	Silmastab AE1527	Silma	1,5	0,6
Hydrophobic MB	Silmastab AX2244	Silma	1,5	0,6
Total filler dosage	-	-	165	61

Example 2: results /1

Fillers (dosage in % of total filler)	8 (%)	9 (%)	10 (%)	11 (%)	12 (%)
Stearic Coated brucite – Ecopiren 3,5C	31	31	31		
Stearic Low-Coated brucite – Ecopiren 3,5LC				31	**37**
Böhmite – Aluprem TB dry	15			15	**12**
Coated böhmite – Aluprem SR100 mes		15	15		
Milled dolomite d50=3		15			
Coated dolomite d50=1,5 (silane)	15		15	15	
Huntite – Portafill H5					**12**
Properties	**8**	**9**	**10**	**11**	**12**
Tensile strenght (MPa)	9,9	10,7	6,2	12,3	**11,1**
Elongation at break (%)	263	152	317	148	**163**
MFI 21,6 kg @ 190°C (g/10min)	13	11	13	12	**10**
LOI (%)	37	36	36	37	**39**

Example 2: results /2

Properties	**8**	**9**	**10**	**11**	**12**
Time 1. Top of the flame 20 cm (s)	105	90	80	120	**240**
Time 2. Bottom of the flame to grad. line (s)	300	270	210	285	**510**
Self extinguish (YES/NO)	NO	NO	NO	NO	**NO**
Presence of burning drops (YES/NO)	**YES**	**YES**	**YES**	**YES**	**NO**
Starting time of burning drops (s)	45	60	45	120	**-**
Dimension of burning drops	small	small	small	small	**-**
Flame height (cm)	30	28	30	27	**18**
Flame width at graduation line (cm)	5	5	6,5	4,5	**4,5**

Industrial HFFR compounds /1

Properties	**ATH 1° phase**	**ATH + nMDH 2° phase**	**nMDH + AOH 3° phase**
Density (g/cm^3)	1,48	1,52	1,51
MFI 21,6 kg @ 190°C (g/10 min)	30	15	5
LOI (%)	38	41	37
Tensile strength (MPa)	13,4	10,8	11,1
Elongation at break (%)	181	176	173
Water absorption test 168h @ 70°C			
Tensile strength variation (%)	-10%	-12%	-11%
Elongation variation (%)	-3%	-25%	-5%
Water absorption (%)	1,3%	2,4%	1,4%
Accelerated ageing in oven 168h @ 100°C			
Tensile strength variation (%)	9%	21%	5%
Elongation variation (%)	-21%	-23%	-25%

Commercial HFFR compounds /2

Group	Parameters	UM	ATH 1° phase	ATH + nMDH 2° phase	nMDH + AOH 3° phase
Flame evolution	Time 1. Top of the flame at high limit (19 cm)	sec	90	225	**185**
	Time 2. Flame base to graduation line (15 cm)	sec	250	375	**425**
Self-extinction	Self-extinction	YES/NO	NO	NO	**NO**
	Time to self-extinction	sec	-	-	**-**
Dripping	Presence of burning drops	YES/NO	**YES**	**NO**	**NO**
	Time to dripping start	sec	60	-	**-**
	Type of dripping	-	Medium burning particles	-	**-**
Flame dimension	Maximal flame height	mm	280	230	**190**
	Flame width at graduation line (maximal width)	mm	70	45	**35**
Solid phase behaviour	Notes	-	Fast ignition Dripping and high deformation of the specimen.	Slow ignition Strong char formation. Small deformation	**Slow to ignite. Close to self-extinguish. Strong char formation**

Conclusions

- Nowadays, a large variety of commercially available and **reliable/consistent mineral fillers** gives to technologists many opportunities to design new types of HFFR compounds.
- **Synergistic combination** of different mineral fillers is a suitable way to comply with the fire regulation and to optimize performances/cost.
- Laboratory scale fire tests are a convenient **preliminary screening** to reasonably predict fire resistant behaviour of the final cable.
- Following a chemiometric approach, IPOOL is collecting massive number of data to create a **quantitative model** («Group Contribution Model») to describe and predict properties of HFFR compounds on the basis of the formulation.